

Observation of multiple Zhang-Rice excitations in a correlated solid: Resonant inelastic X-ray scattering study of Li_2CuO_2

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Abstract – Multiple Zhang-Rice type spectral features have been observed in resonant inelastic X-ray scattering (RIXS) from the quasi-one-dimensional cuprate charge transfer insulator Li_2CuO_2 . The first feature appears at constant emission energy, and is associated with a Zhang-Rice singlet final state. The second is an interplaquette charge transfer excitation that results in a novel triplet Zhang-Rice-type final state. It is accompanied by the presence of a O $2p$ nonbonding to upper Hubbard band excitation at an energy close to that of a calculated triplet charge transfer Zhang-Rice-type excitation. The site selectivity and polarization rules associated with RIXS allows these two excitations to be distinguished.

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The observation of Zhang-Rice singlet (ZRS) states in cuprate high-temperature superconductors and their parent materials has recently been reported [1–3]. These bound hole pairs are thought to play an important role in cuprate superconductivity. There is thus significant interest in understanding the behavior of the ZRS in cuprates. Quasi-one-dimensional cuprate insulators such as Li_2CuO_2 are good candidates for the study of such hole pairs under simplified conditions. Li_2CuO_2 is composed of parallel ribbons of edge-sharing Cu-O squares, or plaquettes, with Li sites between adjacent ribbons, as illustrated in fig. 1(a) [4]. Although the structure appears quasi-one-dimensional, the 94° O-Cu-O bond angle along the ribbons permits only weak hopping between plaquettes, which can be considered largely electronically isolated [4–6]. Each plaquette contains 2 O^{2-} sites and 1 Cu^{2+} site, provided each Li atom is considered a passive donor. Thus each plaquette holds one valence hole on a half-filled Cu $3d$ state. Strong on-site Coulomb repulsion in

the half-filled Cu $3d$ state drives the insulating behavior in Li_2CuO_2 . The effective on-site Coulomb repulsion is larger in Li_2CuO_2 than the charge transfer energy, so Li_2CuO_2 is a charge transfer (CT) insulator [6–9]. The measurement of the electronic structure of insulators using ionizing spectroscopies such as photoemission is problematic due to sample charging [10]. However, resonant inelastic X-ray scattering (RIXS) is a non-ionizing probe of excitations across the Fermi level (E_F) [11]. RIXS not only measures the energy of these excitations, but can also identify which atomic sites are involved in the excitation.

In edge-sharing cuprate insulators, two classes of Zhang-Rice excitations have been predicted (see fig. 1b). The first, observed in RIXS spectra from CuGeO_3 [12], is the result of the excitation of an O $1s$ core electron to a delocalized state above E_F . There is then a finite probability that the delocalized electron will not recombine with the core hole, instead allowing a valence electron to fall into the core hole. If the valence electron is initially in the appropriate O $2p$ state, a Zhang-Rice singlet (ZRS) final state may result. Such an excitation will be referred to as a fluorescence-type ZRS, since in RIXS it appears

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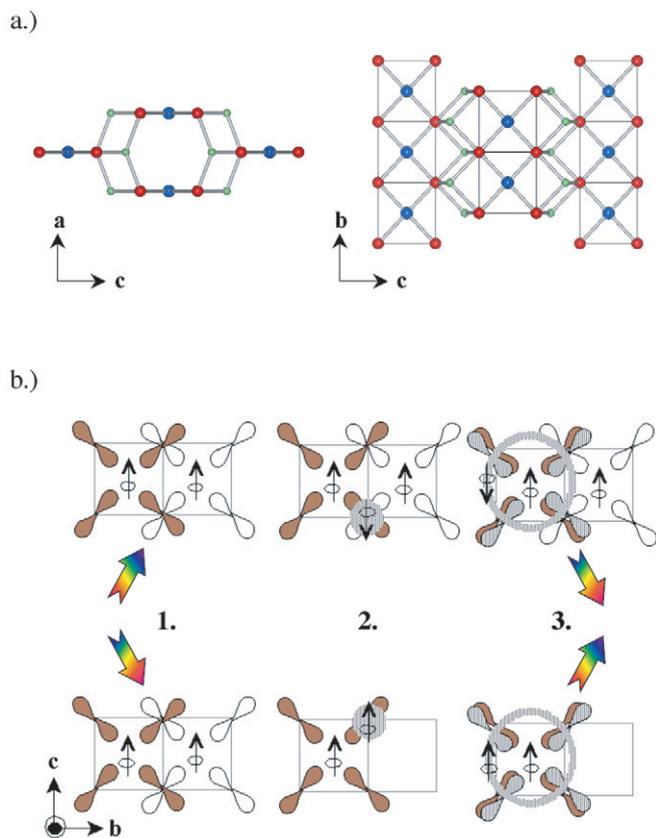


Fig. 1: (Colour on-line) (a) Crystal structure diagram of Li_2CuO_2 . Square outlines denote CuO_6 plaquettes, with blue Cu and red O. Li sites are shown between plaquette chains. (b) Two Zhang-Rice-type excitations. The top panels represent a fluorescence-type (ionizing) Zhang-Rice singlet, the bottom panels represent a charge-transfer-type (non-ionizing) Zhang-Rice triplet. The circled arrows represent the spin of either a valence hole or an O $1s$ core hole. The delocalized O hole is represented by the ring with shaded lobes, the Cu $3d$ holes by a bare circled arrow, and the core hole by a shaded circle. 1. An incident X-ray above (top) or below (bottom) the ionization threshold is absorbed by an O $1s$ electron. 2. The O $1s$ core hole reflects the spin of the state into which the O $1s$ electron was absorbed. 3. An electron from either the plaquette not participating in the absorption (bottom) or either plaquette (top) decays into the O $1s$ core hole, resulting in a Zhang-Rice-type final state.

at a constant emission energy. The fluorescence-type ZRS is analogous to ZRS features observed using photoemission spectroscopy, since the excitation leaves the participating plaquette with one less electron in the final state than in the initial state [13]. Although to the authors' knowledge only spin singlet fluorescence-type final states have been observed in RIXS, in principle the final state could also be either spin singlet or spin triplet [14]. The second class of Zhang-Rice excitation was predicted by Okada and Kotani, and is the result of charge transfer from one plaquette to a neighboring plaquette [15]. This occurs when an O $1s$ core electron is excited into the upper Hubbard band (UHB), but the subsequent core

hole decay involves a valence electron from an *adjacent* plaquette. The result is the transfer of a valence hole from one plaquette to an adjacent plaquette, with the possibility of a Zhang-Rice type final state. In this case, spin conservation rules through the scattering process determine the spin of the Zhang-Rice final state. This type will be referred to as a scattering-type ZR excitation, since in RIXS spectra it appears at a constant energy loss relative to the energy of the photons used to excite the O $1s$ core electrons. The scattering-type ZR excitation conserves the sum of the number of electrons on both of the participating plaquettes.

We report here the results of a high-resolution RIXS study of Li_2CuO_2 at the O K -edge and the Cu L -edge. We observe two low-energy scattering features, and one constant emission energy feature that appears when excitation energies are used that are approximately 4 eV above the O K -edge absorption onset. The low-energy excitations are interpreted in the context of recent experimental and theoretical results [7,16]. The constant emission energy feature is split from the high-energy edge of the O $2p$ main emission peak by approximately 1 eV. It has no analog in other Li_2CuO_2 studies, and is identified as a fluorescence-type Zhang-Rice singlet.

X-ray absorption spectroscopy (XAS) measurements were performed on beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. XAS spectra were recorded in either total fluorescent yield (TFY) mode, with the fluorescence yield measured using a channeltron positioned 25° directly above the incident X-ray beam, or in total electron yield (TEY) mode by measuring the sample drain current. O K -edge and Cu L -edge absorption spectra were calibrated to those previously published for Li_2CuO_2 [8]. O K -edge XAS spectra were taken with 0.2 eV resolution, and Cu L -edge spectra with 0.5 eV resolution. All RIXS measurements were taken using a Nordgren type compact spherical grating X-ray spectrometer [17,18]. The O K -edge emission was calibrated to metallic Zn $L_{\alpha 1,2}$ and $L_{\beta 1}$ emission lines in second order, and Cu L -edge emission was calibrated to metallic Cu $L_{\alpha 1,2}$ and $L_{\beta 1}$ emission lines. The RIXS measurements were undertaken at three separate beamlines: X1B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory; beamline I511-3 at the MAX-lab synchrotron radiation facility in Lund, Sweden; and at beamline 7.0.1 at the ALS. For the O K -edge, all RIXS measurements were performed with an incident photon energy resolution of 0.3 eV and a spectrometer resolution of 0.4 eV. For the Cu L -edge RIXS, both the incident photon energy and the spectrometer resolution were set to 1 eV. All of the data presented here were recorded with the spectrometer in the plane orthogonal to the incident X-ray beam.

The results of measurements taken with the incident X-rays polarized along the b crystal axis, which is parallel to the Cu-O ribbons, are shown in fig. 2. The top panel shows the O K -edge XAS (TFY) spectrum. The peak

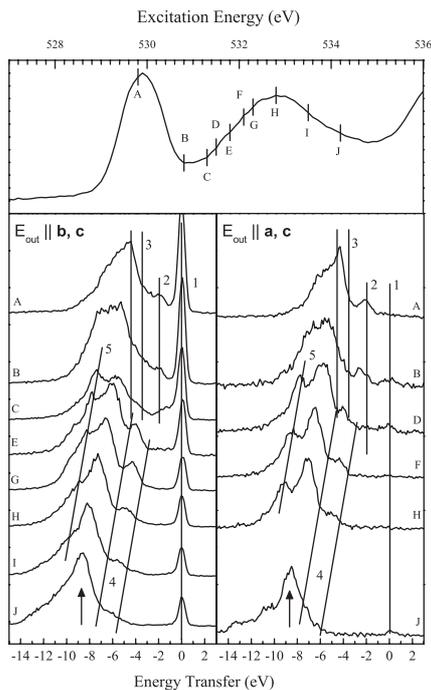


Fig. 2: XAS (TFY) and RIXS spectra recorded at the O K -edge. RIXS excitation energies are marked with bars on the XAS spectrum (top panel). The RIXS spectra in the lower panels were recorded with the incident X-ray polarization parallel to \mathbf{b} , and the spectrometer positioned parallel to the \mathbf{a} (left) and \mathbf{b} (right) crystal axis. The vertical offset of each spectrum is proportional to the change in excitation energy relative to spectrum A. The strongest peak in the two spectra marked J corresponds the O $2p$ nonbonding fluorescence feature at 525.6 eV. Feature 1 denotes the elastic peak, and feature 2 the d - d excitation. The box marked feature 3 encloses the ZRT feature. Feature 4 marks the ZRS fluorescence. Feature 5 marks the Li associated resonance.

centered near 530 eV is due to absorption into the UHB, and is composed of strongly hybridized O $2p$ states and Cu $3d$ states [19]. The broad higher energy peak is due to absorption into O $2p$ states hybridized with unoccupied Li $2s$ and $2p$ states [7,8]. The states in the UHB are quite localized on the plaquettes, but the Li hybridized states are less confined to the Cu-O ribbons. Thus we expect strong Cu-O related RIXS features when exciting into the UHB, but not at higher energies when the intermediate RIXS state involves the hybridized Li states. The excitation energies used to produce the RIXS spectra shown in the bottom panels of fig. 2 are marked on the XAS spectrum, and RIXS features are marked in both of the bottom panels. Feature 1 is elastic emission and appears at an energy loss of 0 eV. At higher loss energies, there are four features that are of particular interest. Feature 2, appears at 2.0 eV loss and is composed of Cu d - d excitations. These are local transitions from the initial d^9 state to a distinct d^{9*} final state. These excitations appear at the O K -edge only when the excitation energy is tuned to an unoccupied Cu $3d$ hybridized state, which

in Li_2CuO_2 is the UHB. This identification corresponds to the predicted crystal field splitting of 2 eV [20], and is in reasonable agreement with similar measurements in this and other cuprate insulators [9,21–23]. Although the difference in the background weight due to other features makes such comparisons difficult, we observe no clear difference in the spectral weight of the 2.0 eV feature between the two different detection geometries. The next two features are marked 3 and 4 in fig. 2. Feature 3 is at a constant energy loss of 4.1 eV. This is lower in energy than the charge transfer excitations seen in Cu K -edge [9] and L -edge (this work) RIXS, and obviously higher in energy than the Cu d - d excitation marked as feature 2. At 4.1 eV, feature 3 appears at an energy that can be assigned to a charge transfer (CT) excitation. However, since the feature is also visible at excitation energies corresponding to more than one intermediate RIXS state, it should be treated as two separate excitations. First consider the feature at excitation energies corresponding to the UHB, which are marked A-C. The energy of the feature is close to the energy difference between the O $2p$ nonbonding band seen in the normal part of the RIXS spectrum at 525.6 eV (see arrow in the bottom panel of fig. 2) and the UHB seen in XAS at 529.9 eV. Also, an intense feature at 4.0–4.5 eV attributed to O $2p$ nonbonding to UHB transitions has been reported in optical conductivity and electron energy loss spectroscopy experiments [6,7]. Thus the feature could originate from an excitation from an O $2p$ nonbonding state to the UHB. However this explanation is not satisfactory as the excitation is only observed in experimental geometries where the incident X-ray polarization vector is parallel to \mathbf{b} . Since each plaquette in Li_2CuO_2 is quite electronically isolated near E_F , we expect the O $2p$ nonbonding to UHB excitation to appear when the X-rays are polarized along *either* \mathbf{b} or \mathbf{c} [24]. Careful O K -edge XAS measurements have shown that X-ray absorption into the UHB occurs with nearly equal intensity for X-rays polarized along the \mathbf{b} - or \mathbf{c} -axis [8]. However, it is also possible that feature 3 is a higher-energy triplet analog of the ZRS scattering excitation discussed earlier. The novel triplet (ZRT) scattering-type excitation is a variation on an excitation predicted by Okada and Kotani [15], where the charge transfer is from one plaquette to an adjacent plaquette, leaving on the first plaquette a two hole bound Zhang-Rice singlet [25]. The ZRT scattering excitation is the same, except the final state is triplet rather than singlet. The triplet final state is the result of valence hole spin alignment between the two participating plaquettes. Both the O $2p$ nonbonding CT and the ZRT excitations are allowed in O K -edge RIXS, but not in Cu L -edge RIXS. For the O $2p$ nonbonding CT excitation, the O $2p$ nonbonding band is only weakly hybridized and not visible in normal RIXS at the Cu L -edge. For the scattering-type Zhang-Rice excitation, the O $1s$ wavefunction overlaps with two neighboring plaquettes, and O $1s$ participation is necessary to open a channel for charge transfer from one plaquette to the next. Since

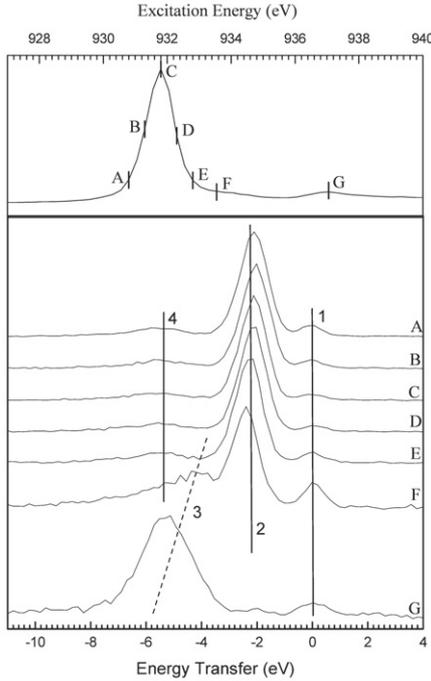


Fig. 3: XAS (TEY) and RIXS spectra recorded at the Cu L_3 -edge. RIXS excitation energies are marked with bars on the XAS spectrum.

for a given Cu atom, all the Cu $2p$ states are contained within a single plaquette, Cu $2p$ states cannot serve the same purpose.

Figure 3 shows Cu L -edge RIXS taken at energies marked in the Cu L_3 -edge XAS (TEY) spectrum shown at the top. Feature 1 is again the elastic peak at 0 eV energy loss. The Cu d - d excitation marked as feature 2 is visible at 2.0 eV, and a 5.4 eV CT excitation is marked as feature 4. Both of these excitations have been reported at the Cu K -edge [9]. In between features 2 and 4, the valence band emerges as feature 3. The valence band is only visible at excitation energies above the UHB, where the d - d excitations are weak. As expected, there is no 4.1 eV excitation visible.

The Zhang-Rice-type process described above was proposed by Okada and Kotani following a cluster model calculation [15,16,26]. In this picture, one can treat each whole plaquette as a site, and consider charge transfer from one plaquette to a neighboring plaquette. Due to the near 90° Cu-O-Cu bond angle in Li_2CuO_2 , the charge transfer must go through an O site, since the O $2p$ -Cu $3d$ hybridized states on a plaquette only very weakly overlap with the same states on an adjacent plaquette. Okada and Kotani [15] predicted that O $1s$ RIXS can instigate the interplaquette charge transfer necessary for this excitation in an edge-sharing cuprate such as Li_2CuO_2 . In their calculation, antiferromagnetic alignment between neighboring Cu sites leads to a final state that is $d^{10}p^6$ on one plaquette, and a d^9p^5 Zhang-Rice singlet on the adjacent one. The final state must be a singlet because

there is only one unoccupied hole per plaquette in the UHB, and the holes reflect the spin of the Cu sites. Antiferromagnetic coupling requires spin anti-alignment of neighboring Cu $3d$ holes along the Cu-O ribbon, and ferromagnetic coupling requires spin alignment. In the X-ray absorption process, the spin of the valence hole determines the spin of the core electron that can be promoted to the valence hole, and so also selects the spin of the O $1s$ core hole. Thus through the O-mediated interplaquette CT process, the spin of the transferred valence hole is preserved. The calculated energy of this novel excitation is 2–2.5 eV, depending on the details of the edge-sharing cuprate compound being measured [15]. Feature 3 in fig. 2 is too high in energy to correspond to this excitation, but Li_2CuO_2 is not purely antiferromagnetically coupled between neighboring plaquettes at room temperature. This reflects the competition between ferromagnetic and antiferromagnetic coupling along the ribbons [7,27]. Thus we expect neither strong alignment nor anti-alignment of the neighboring valence holes, so the final state of the excitation can be either $d^{10}p^6 + d^9p^5$ singlet or $d^{10}p^6 + d^9p^5$ triplet. We must then consider the higher-energy triplet excitation [25]. Following a three-band Hubbard model calculation by Simón and Aligia, [14] and taking $\Delta = 3.2$ eV, $U_d = 8.5$ eV, and $t_{pp} = 0.5$ eV [7] we find a rough estimate of the singlet-triplet energy separation at 2.5 eV. This places the ZRT excitation at 4.5–5 eV. We interpret the part of feature 3 in spectra A-C as primarily resulting from an interplaquette CT excitation resulting in a Zhang-Rice triplet final state. This picture relies upon tuning the O K -edge excitation energy to the UHB (which is strongly Cu $3d$ -O $2p$ hybridized) to couple the two adjacent plaquettes.

As noted earlier, the peak near 533 eV in the O K -edge absorption spectrum (fig. 2) is due to absorption into unoccupied Li $2s$ and $2p$ states hybridized with O $2p$ states. The strong increase in RIXS intensity observed in feature 4 at this excitation energy is unexpected, and indicates that electrons in the corresponding unoccupied state are not as itinerant as initially assumed. Following an LDA calculation by Neudert *et al.* [8], the O $2p$ component of the state is primarily of $2p_z$ character, which is in our coordinates along the \mathbf{a} -axis. However, the incident X-ray polarization along \mathbf{b} in our data suppresses p_z -related spectral weight. Thus the sharp increase in the intensity of feature 4 in spectrum *E* and spectrum *F* may be related to an O $2p$ orbital hybridized with another state, such as the Cu $4p$. As the excitation energy is increased further, the ionization threshold is crossed and excited core electron is no longer strongly involved in the core hole decay process. Thus now the absorption process removes an electron, and the fluorescence-type ZRS final state is possible. This is identified as feature 4. Feature 5 is a state in the valence band that resonates quite broadly over the entire absorption edge, with a maximum near the low-energy side of the Li hybridization peak. The width of the

resonance covers a number of different intermediate states, extending over both Cu-O states and Li-O states. Thus the resonance is not clearly attributable to the symmetry of the intermediate core-excited state [28].

In conclusion, the RIXS data presented above indicate that there is a two-hole bound state in Li₂CuO₂. We observe features due to Cu *d-d* excitations, a Zhang-Rice singlet final state, and another feature that is tentatively attributed to a local triplet excitation. All of these features are characteristic of strong electron correlation, and provide evidence of the localization of the electronic states near E_F . The site-specificity of RIXS can be used to directly measure the involvement of different elements in the measured excitations.

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